Plasma electrolytic oxidation of titanium in a phosphate/silicate electrolyte and tribological performance of the coatings

S. Aliasghari, P. Skeldon*, G.E. Thompson

Corrosion and Protection Group, School of Materials, The University of Manchester, Manchester M13 9PL, UK

1. Introduction

Plasma electrolytic oxidation (PEO) is being studied extensively as a method of coating light alloys, especially for wear resistance, corrosion protection and biocompatibility [1–9]. The coatings are formed by polarizing the metal to the dielectric breakdown voltage in a suitable electrolyte. A wide range of polarization conditions are available for formation of the coatings, including DC and AC, with control of the current, voltage or power supplied to the cell. Under AC conditions, a variety of waveforms and frequencies can be employed. The coatings can be formed to many microns in thickness and are composed of species derived from the substrate and the electrolyte in amounts dependent upon the conditions of coating formation. The coating material is generated at the sites of microdischarges on the polarized metal that give rise to very high local current densities, temperatures and pressures [10,11]. Several types of discharge may occur, with different optical emissions and influences on the composition of the coating [12–14]. Thus, it has been suggested that discharges that occur near the coating surface may incorporate more species from the electrolyte than those that occur deeper in the coating. The nature of the discharges can also change during the PEO process, leading to large changes in the morphology of the coating [12–14]. Owing to the nature of the coating growth, the coating material contains numerous pores, which are formed by the discharge channels and the relatively vigorous gas evolution that accompanies the growth of the coating [15]. The localized heating can melt the coating material and, possibly, the metal in the vicinity of the discharges, with cracks forming in the coating as it cools [16]. However, a barrier layer, <1 μm thick, is often present next to the metal, which may be the main source of corrosion protection of the substrate [17]. The high temperatures that are reached locally in the coating allow the formation of a variety of crystalline and amorphous phases. The crystalline phases can give rise to coatings of high hardness and wear resistance. The mechanism of coating material formation remains the subject of discussion, but it is likely to involve several processes, including anodic oxidation, thermal oxidation, thermolysis, and reactions of substrate and electrolyte species within the plasmas generated by the discharges.

In the case of titanium and titanium alloys, PEO coatings have been of particular interest for improvement of the tribological behaviour and of the biocompatibility of the substrates. A wide variety of forming conditions have been investigated, producing films of differing compositions, morphologies and thicknesses. Shokoufar et al. formed coatings of a few microns thickness on titanium, using pulsed DC at 350 V, a frequency of 1000 Hz, a duty cycle of 40% and a treatment time of 3 min [18]. TiAl2O5 and anatase were present in coatings grown in an aluminate electrolyte, and anatase and rutile were present in coatings formed in other electrolytes. Kuramoto et al. formed coatings up to 1.7 μm thick in phosphoric acid, using constant voltages in the range 50–250 V [19]. Hu et al. formed ~10 μm thick coatings that contained anatase and...
zinc species under unspecified electrical conditions. The coatings were considered candidates for orthopaedic and dental implants [20]. Chu et al. grew coatings in a phosphate electrolyte under a unipolar pulsed DC voltage of 490 V for 1 h. The coatings contained anatase, a small amount of rutile, and also amorphous material [21]. Zhang et al. prepared coatings containing anatase and rutile in a silicate electrolyte containing Na₂[EDTA], CaO and Ca(H₂PO₄)₂, using 350 V pulsed DC, at a frequency of 200 Hz, a duty cycle of 50% and a treatment time of 5 min [22]. Incorporated silicon species increased the rate at which apatite formed during immersion of the coated substrate in simulated body fluid.

Other studies have examined PEO of Ti-6Al-4V titanium alloy. Wang et al. employed either a constant rms voltage (500 V) or a constant rms current density (60 mA cm⁻²) in a silicate/hexametaphosphate electrolyte at either 600 or 100 Hz, with a duty cycle of 8% or 1% [23]. Under constant current density, a coating thickness of ~90 μm was produced after 90 min. Under constant voltage, the growth rate decreased with time. The coatings contained anatase and rutile, with the latter increasing with time. Yao et al. employed a phosphate/aluminate electrolyte, with a current density of 20 mA cm⁻², a pulse frequency of 2 kHz, and a duty cycle from 10% to 45% [24]. The coating thickness, which was in the range ~10 to 20 μm, tended to increase with the duty cycle. The coatings revealed two sizes of pores, with the diameter of the pores increasing and the population density decreasing as the duty cycle increased. The coatings contained Al₂TiO₅ and a small amount of γ-Al₂O₃. The authors repeated the study using a frequency of 500 Hz [25]. The coating thickness increased with duty cycle, from ~13 μm at 10% to ~38 μm at 45%. A duty cycle of 45% led to the roughest coating, which contained finer and fewer pores. At a duty cycle of 10%, the coating contained a large amount of Al₂TiO₅. In contrast, at a duty cycle of 45%, γ- and α-Al₂O₃ were dominant. Khorasani et al. carried out PEO at 380 V DC for 10 min in an electrolyte containing NaCl, NaOH, Na₂SiO₃, H₂O₂ and starch [26]. The resultant coating was 48 μm thick, with a two-layered, dense structure. The coating was composed of rutile, anatase and non-stoichiometric titanium(II) oxide. Starch increased the coating thickness, improved the coating adhesion and reduced the porosity. Montazeri et al. used pulsed DC (in the range 350–500 V) in a calcium acetate, sodium dihydrogen phosphate hydrate electrolyte, with a frequency of 1000 Hz and a duty cycle of 40% for 1.5–20 min [27]. Brookite and rutile were detected in the coatings at all voltages, and anatase at lower voltages. Hydroxyapatite was also found at 500 V. Yerokin et al. investigated coatings formed under constant anodic power density in several different compositions of electrolyte, finding coatings produced in an aluminate-phosphate electrolyte provided the highest wear resistance, although with a relatively high coefficient of friction [28]. These coatings contained Ti₆Al₂O₅ and rutile. The coatings were relatively dense and uniform, whereas coatings formed in a silicate electrolyte were porous and contained amorphous and crystalline silica and TiO₂.

Porous structures in anodic coatings are potentially favourable for the addition of material that improves the surface properties, for example a solid lubricant material, such as polytetrafluoroethylene (PTFE), or a secondary coating. For example, Zou et al. incorporated fluoropolymer particles into a porous alumina film by either hot-dipping or electroplating deposition [29]. Liu et al. synthesized hard anodic coatings containing PTFE particles on AA 6063 aluminium alloy by adding the particles to the electrolyte [30]. Kuang et al. showed that combinations of metal oxide particles and PTFE can provide both high microhardness and good self-lubricating properties [31]. Various particles, such as oxides, clay and PTFE, have been incorporated into PEO coatings on aluminium and magnesium to improve the properties of the coatings [32–40]. Rudnev et al. incorporated PTFE into PEO coatings formed on an aluminium alloy under galvanostatic conditions [37,38]. The silicate-based electrolyte contained dispersed solid PTFE and siloxane–acrylate emulsion. High loadings of PTFE resulted in the contact angle between the coating and water droplets being similar to that using bulk PTFE. A relatively high ratio of carbon to fluorine in the coatings suggested that the PTFE was partially degraded during PEO. A similar approach was used to form coatings that contained graphite particles on a titanium alloy [37]. PTFE has also been applied to PEO-coated titanium in post-treatments to reduce scaling of heat exchangers [41] and to reduce the wear and friction of PEO coatings on Ti-6Al-4V alloy [42].

Most of the previous studies of PEO of titanium and titanium alloys have employed either a single condition or a limited range of conditions for preparation of the coatings. The conditions cover a wide range of electrical regimes, electrolyte compositions and treatment times, which makes it difficult to identify the influences of specific processing parameters on the formation of the coatings. In the present work, PEO has been carried out on titanium under a relatively wide range of duty cycle, current density, waveform and treatment time in an alkaline phosphate/silicate electrolyte in order to identify whether or not these parameters have a significant influence on the composition, structure and morphology of the coatings. Further, the incorporation of PTFE into the coatings to improve the friction behaviour and wear resistance is investigated, revealing a reduction in the coefficient of friction of the coating against a steel counterface.

2. Materials and methods

2.1. Material and PEO conditions

Commercial purity 99.6% titanium sheet, of 1.0 mm thickness, was obtained from ADVENT Research Materials Ltd., England. The composition of the titanium according to optical emission spectroscopy (OES), which analyzed the metallic constituents of the titanium, is given in Table 1. Rectangular specimens were cut from the sheet and ground to a 1200 SiC grade finish. They were then degreased with acetone, washed with distilled water, dried in air at 40°C and, finally, coated in lacquer (Stopper 45 MacDermid), leaving working areas of ~1.0 cm². AC PEO treatment was carried out at a constant rms current density with a square waveform, employing different negative to positive (peak-to-peak) current ratios (iₘ/iₚ), using an ACS-FB power supply (ET systems electronic GmbH). The frequency was 50 Hz, with a duty cycle in the range 30–70%. An aqueous electrolyte was prepared by dissolving reagent grade sodium silicate (10.5 g l⁻¹ specific gravity 1.5), phosphoric acid (2 ml l⁻¹) and potassium hydroxide (2.8 g l⁻¹) in deionized water. The conductivity and pH of the electrolyte were 10.2 mS cm⁻¹ and 12.2 respectively. The electrolyte, of volume 1 dm⁻³, was stirred with a magnetic stirrer during PEO. A double-walled glass cell was employed to contain the electrolyte. The temperature of the electrolyte was kept at 25°C by a flow of cold water through the cell wall. A stainless steel (type 304) plate of dimensions 7.5 × 15 cm was used as a counter electrode. The applied current density was in the range 200–900 mA cm⁻² (rms), with treatment times of up to 3600 s. Voltage (rms)–time responses were recorded electronically during anodizing, employing LabView software with a sampling time of 20 ms. The data acquisition system for monitoring of the voltage employed National Instruments (NI) SCXI high-performance signal conditioning and switching platforms. The set-up included two isolation modules with terminal blocks installed in the SCXI-1000 chassis. The first module had a NI TBX-1316 terminal block connected to it. The second one had an SCXI-1328 terminal block. The TBX-1316 is a high voltage attenuator terminal block for analogue input modules. The NI TBX-1316 is designed to divide by
200 the input AC/DC voltage signals in the range up to 1000 V. The SCXI-1328 does not change the input signal; its maximum input voltage is 5 V. A shunt resistor of 1 Ω was installed into the electric circuit to enable the acquisition of the current using the SCXI-1328, which allows measurement of a maximum current of 5 A.

Light emission of the discharges was collected using an optical emission spectroscope (USB4000 Ocean Optics), with an optical fibre immersed in the electrolyte, and located a few centimetres from the specimen to optimize the collected light intensity and to reduce absorption from the bath. The polarisation-resistant optical fibre (ZFQ-9596, Ocean Optics), with PVDF sleeving and a PEEK ferrule, was of 1000 μm diameter, with a numerical aperture of 0.22 ± 0.22. Emission spectra were recorded in the wavelength range 200–850 nm with a spectra resolution of 1 nm.

2.2. Specimen examination

PEO-treated specimens were examined in plan view and cross-section using Zeiss Evo 50 and Zeiss Ultra 55 scanning electron microscopes, equipped with energy dispersive X-ray (EDX) analysis facilities. Cross-sections were ground through successive grades of SiC paper, followed by finishing with 1 μm diamond paste. Fabrication of electron-transparent (∼80 nm thick) sections for transmission electron microscopy (TEM) of a PEO-coated specimen was carried out using a FEI Nova Lab dual beam focused ion beam (FIB) facility. The section was examined using a TECNAI F30 G2 instrument, operated at 300 kV, with a Gatan imaging filter (GIF2001). Phase composition was investigated by X-ray diffraction (XRD), using a Philips X’Pert-MPD (PW 3040) instrument with copper Kα radiation, a step size of 0.005° and a scan range from 5° to 85° (2θ).

The wear behaviour of the coated and uncoated titanium was studied using a ball-on-disc apparatus, using a 5 N load, a rotation rate of 20 rpm and a track diameter of 5 mm. The ball, of 3 mm diameter, was made from AISI 52100 steel of nominal composition (by wt) Cr 1.3–1.6%, C 0.98–1.1%, Mn 0.25–0.45%, Si 0.25–0.30%, S ≤0.025%, P ≤0.025%, Fe bal. The coatings were formed for 900 s at 500 mA cm−2, with a duty cycle of 50 Hz and Δu/Ip ratio of 1. This condition produced the most uniform coatings for the range of formation conditions that were investigated. For growth of selected coatings, 5 g l−1 of a commercial emulsion containing 60 wt% of ptfe particles of size from ~150 to 550 nm and 5 wt% fibrillar carbon of length up to ~800 nm and width of ~150 nm were added to the electrolyte. These coatings were formed at 500 mA cm−2, with a duty cycle of 50% and an Δu/Ip ratio of 1. Incorporation of ptfe into coatings was evaluated by thermogravimetric analysis (TGA), employing a NETZSCH STA 449 C instrument. The measurements were performed on a 10 mg sample of a coating that was heated at a rate of 10 °C/min from 25 to 1000 °C in sealed Al2O3 pans under a N2 atmosphere. Comparison was made with the dried ptfe emulsion and with coatings not containing ptfe. In order to remove the liquid phase, the emulsion was heated to 150 °C and held at this temperature for 3 h. The dried material comprised 68% of the initial weight of the emulsion. The coatings were scraped with a razor blade to remove material for testing. Analysis of the dried ptfe emulsion using a C, S analyzer (ELTRA) in the presence of oxygen indicated that free carbon represented 5% of the initial weight of the emulsion. The remaining 3% of solid is possibly residues of surfactants.

3. Results and discussion

3.1. Voltage–time response

Fig. 1(a) presents the voltage–time response during PEO of titanium for 3600 s at a current density of 500 mA cm−2 with a duty cycle of 50% and an Δu/Ip ratio of 1. The voltage first rises rapidly to ~310 V as a barrier-type anodic film is formed and sparking commences. It then decreases by ~10 V to a shallow minimum at ~200 s and recovers to ~310 V at ~500 s accompanied by increasing oscillations. A steep drop to ~160 V occurs at 900 s followed by a recovery to ~215 V at 1200 s, with fluctuations of up to ~10 V about this value until the treatment ends. The acoustic emission from the discharges reduced significantly following the voltage drop compared with the earlier period of treatment. Numerous, fine, white

![Image](http://example.com/image1.png)

**Fig. 1.** (a) Cell voltage during PEO of titanium for 3600 s at 500 mA cm−2, with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratio of 1. Inset: photographs of specimens after PEO for 180 and 700 s. (b) Scanning electron micrograph (secondary electrons) of the titanium surface at a dark region of the inset image at 180 s of (a).
sparks occurred initially. The sparks first appeared around the edge of the working area, but rapidly spread to all regions. Their size and brightness increased with time and their colour developed an orange hue at approximately the time of the shallow minimum voltage at \( \sim 200 \) s. Thereafter, they became increasingly large, with regions of brightness of up to \( \sim 1 \) mm in size being visible by the unaided eye as the voltage rose to the maximum at \( \sim 500 \) s. Beyond the maximum voltage, the sparks became progressively fewer and smaller as the voltage gradually diminished, and sparking ceased for \( \sim 300 \) s during the large voltage drop and the gradual recovery. The sparking re-commenced, but with fewer and smaller sparks, which were of orange hue, compared with earlier times. Gas evolution occurred throughout the PEO process. The specimen was dark grey when sparking commenced. White coating material then formed around the edge of the working area and in spots elsewhere, (see inset in Fig. 1(a)), which subsequently spread to all regions by the time of the voltage drop. Fig. 1(b) shows a secondary electron scanning electron micrograph of the surface of a specimen before the formation of the white coating material, which later results indicate consists mainly of amorphous silica. The coating contains numerous pores of size up to \( \sim 1 \) \( \mu \)m diameter. Examination of a cross-section of the specimen (not shown) revealed that the coating was \( \sim 1 \) to \( 2 \) \( \mu \)m thick. The pores are formed by dielectric breakdown of the coating and evolution of gas from the coating. The dielectric breakdown may be initiated by electron injection and subsequent avalanching or by thermal runaway of current [43–45]. Local heating, melting and possibly vapourization of the film lead to formation of a discharge channel, generation of a plasma and optical and acoustic emissions. With regard to the generation of oxygen, it is well-known that barrier-type anodic films on titanium undergo an amorphous-to-crystalline transition at relatively low voltages, dependent upon the particular conditions of film growth [46,47]. Oxygen is then generated within the film at locations of crystals, forming bubbles of oxygen gas within the film [47]. The gas is eventually released when the film ruptures, leaving an open pore.

Similar voltage–time behaviours and appearances of specimens to those shown in Fig. 1 were observed at duty cycles of 60% and 70%, although with small increases in the maximum voltage. Conversely, at a duty cycle of 40%, the voltage declined steadily from the sparking voltage and sparks ceased after \( \sim 700 \) s, when the voltage dropped quickly to \( \sim 20 \) V. At duty cycles above 70%, the process was terminated after short times, due to the severity of the sparking processes, large voltage fluctuations and loud acoustic emission.

The effect of changing the \( i_{\text{in}}/i_{\text{p}} \) ratio, at a duty cycle of 50%, is shown in Fig. 2(a). For ratios from 1 to 1.13, the behaviour resembled that of Fig. 1, with a rapid rise to 290–300 V, a small decrease and recovery over the next \( \sim 500 \) s, a large drop to 130–160 V at \( \sim 800 \) s, and recovery to 200–220 V at 1200 s. At ratios from 1.16 to 1.23, the response departed from the previous one after \( \sim 200 \) s, when the voltage either increased slightly, at a ratio of 1.16, or declined slowly, at ratios 1.20 and 1.23, and then dropped to \( \sim 30 \) to 45 V when sparks ceased.

The authors also investigated coating formation at current densities in the range 200–900 mA cm\(^{-2}\), using a duty cycle of 50%, an \( i_{\text{in}}/i_{\text{p}} \) ratio of 1 and a treatment time of 900 s. At a current density of 200 mA cm\(^{-2}\), the voltage remained low, only reaching a maximum value of \( \sim 8 \) V. Gas evolution was observed at the surface of the specimen, which remained of metallic appearance. SEM examination revealed a faceted surface (not shown), indicating etching of the titanium by the treatment. The etching is presumed to be associated with the heating and the changes of pH of the electrolyte near the specimen surface during PEO that resulted in thinning of the oxide film on the titanium surface. The voltage–time behaviours for specimens treated at current densities from 300 to 900 mA cm\(^{-2}\) are displayed in Fig. 2(b). The behaviours at current densities of 300 and 500 mA cm\(^{-2}\) were similar. At higher current densities, the voltage at the onset of sparking was increased and thereafter showed greater fluctuations than at lower current densities. The coatings formed at current densities from 300 to 900 mA cm\(^{-2}\) were of a similar white appearance to those formed at 500 mA cm\(^{-2}\).

### 3.2. Optical emission spectroscopy

Fig. 3(a) displays the optical emission spectra recorded at intervals of 60 s during PEO for 900 s at a current density of 500 mA cm\(^{-2}\), with a duty cycle of 50% and an \( i_{\text{in}}/i_{\text{p}} \) ratio of 1. Emissions were detected initially from mainly titanium (Ti I 307.8 nm), hydrogen (H\(_{\alpha}\) 656.3 nm, H\(_{\beta}\) 486.1 nm, sodium (Na I 589.6 nm) and silicon (Si I 288.1 nm) species derived from the titanium substrate and the electrolyte. Small peaks were also present due to potassium (K I 766.5 and 769.9 nm) and oxygen I (777.1 nm), originating from the electrolyte. Fig. 3(b) and (c) shows that the peaks for titanium, silicon and hydrogen species reduced in height with time. The voltage–time response in the inset of Fig. 3(b) was recorded during the measurements. A particularly large reduction of the titanium peak occurred after \( \sim 300 \) s, which is close to the shallow trough in the voltage response, when the sparks also changed in colour with the development of an orange hue. In contrast, the peaks for sodium and potassium increased by a factor of \( \sim 2.5 \) during the first 540 s, when the maximum emission intensities were reached. After
780 s, at the start of the voltage drop, only peaks of sodium and hydrogen-α were resolved.

3.3. Kinetics of coating formation

The dependence of the coating thickness on the time of PEO at 500 mA cm\(^{-2}\), with a duty cycle of 50% and an \(i_0/i_p\) ratio of 1 is shown in Fig. 4, using thicknesses measured by the eddy current meter and by SEM of coating cross-sections. The thicknesses were determined by the eddy current method only for those specimens that were covered uniformly by the white coating material, which occurred at times from 700 s. The measurements by SEM apply also to the white coating that formed locally at earlier times. Both methods of measurement indicated a thickness of \(~30 \mu m\) after 900 s,
corresponding to an average growth rate of \( \sim 33 \text{ nm s}^{-1} \). Thereafter, the growth rate slows, with the thickness after 1800 s reaching between 40 and 50 \( \mu \text{m} \). After this time, the growth rate remained relatively constant or slightly decreased. The eddy current method indicated a greater thickness at relatively long treatment times than SEM, which is probably due to the coating roughness that is shown in later scanning electron micrographs. The eddy current method also samples a relatively large area of the specimen surface, contrasting with the localized measurements obtained from the cross-sections observed by SEM. Since the rate of coating growth was negligible after \( \sim 1800 \text{ s} \), further studies were confined to treatment times of either 900 or 1200 s.

Other work has reported a similar declining rate of coating growth on a Ti-6Al-4V alloy in a silicate-hexametaphosphate electrolyte, with the rate of thickening at long times of treatment becoming very low, similar to the present observation; the slow growth correlated with the initial microdischarges being replaced by arcs and with increase of the coating roughness [23].

The voltage-time and optical emission behaviours of Figs. 1 and 3 are similar to the findings for PEO of aluminium and magnesium alloys, in which there is a transition to a “soft” sparking regime, treated under similar current densities to those of the present work [13,48]. For aluminium and magnesium, a drop in voltage occurs at the time of the transition and, simultaneously, the acoustic emission from the discharges and the optical emission from the metal species decrease [12,13], as observed for the titanium in the present work. At the same time, the coating material becomes less porous and more uniform in thickness, with the thickness significantly increasing under the new sparking regime, thus generating coatings with properties more suitable for wear-resistant applications. However, in the present instance, the coating growth is significantly slowed following the voltage drop and, as will be evident from later SEM investigations of the coatings, no beneficial changes in the coating composition and morphology resulted.

3.4. Coating morphology and composition

Fig. 5(a) shows a scanning electron micrograph of the surface of a coating formed for 900 s at 500 mA cm\(^{-2}\), with a duty cycle of 50\% and an \( \text{in}/\text{off} \) ratio of 1, revealing protrusions of coating material of sizes up to tens of microns that result in a relatively rough coating surface. The composition of the surface region according to EDX point analysis (in at\%\) was 70\% O, 23\% Si, 3\% P, 3\% Ti, <1\% K and <1\% Na, suggesting that SiO\(_2\) is the main constituent. The cross-section of Fig. 5(b) shows that the coating thickness ranges from \( \sim 25 \) to 40 \( \mu \text{m} \). Numerous pores, with sizes from \(-0.1\) to 10 \( \mu \text{m} \), are present throughout the coating. Contrast variations in apparently more compact regions are due to buried pores. The EDX elemental maps of Fig. 6 show that silicon and oxygen are present in most parts of the coating, while titanium mainly occurs in a \( \sim 7 \mu \text{m} \) thick region next to the substrate, where phosphorus is also enhanced. Sodium and potassium are minor or negligible constituents of most regions of the coating. A relatively similar nodular morphology of the coating surfaces and the presence of large amounts of silicon have been reported for a Ti-6Al-4V alloy treated using a commercial power source in a silicate-phosphate electrolyte and for DC PEO of titanium in a silicate electrolyte [49,50]. The silicon-rich material is probably composed mainly of amorphous silica that is deposited due to either changes in pH of the electrolyte near the coating surface, oxidation of silicate ions or thermolysis of the electrolyte. Coatings formed for longer times, up to 3600 s, or formed at a current density of 300 mA cm\(^{-2}\) for 900 s had morphologies generally similar to that shown in Fig. 5, although formation for 3600 s increased the roughness of the coating surface.

A bright field transmission electron micrograph of the outer region of the coating is shown in Fig. 7(a). The section, which was prepared by FIB milling, shows regions of different contrast that result from differences in the composition and/or thickness of the section. The coating reveals numerous pores, typically from 20 to 500 nm in diameter. EDX maps indicate that the coating contains oxygen, titanium, silicon, phosphorus and potassium species. Mapping of carbon indicated that the pore-free regions of light contrast consist of resin used to mount the specimen. Fig. 7(b) shows details of the circled region of Fig. 7(a), revealing nanocrystals; the electron diffraction patterns of Fig. 7(c) indicated the presence of rutile.

Fig. 8 shows a transmission electron micrograph of the innermost 400 nm of the coating and the underlying titanium substrate and EDX elemental maps of the section. Most regions of the coating contained titanium, oxygen and phosphorus. No significant amounts of potassium and sodium were detected and, hence, maps for these elements are not shown. Silicon was concentrated around the peripheries of the pores, with smaller amounts in the main body of the coating. The pores were usually approximately circular, with size up to 70 nm. An elongated pore or crack was also present in the section, near the titanium/coating interface, although this may be an artefact of the preparation of the section. An EDX point analysis of the coating material revealed mainly titanium and oxygen, with lower amounts of phosphorus and silicon and negligible amounts of potassium and sodium.

Fig. 9 displays a bright field transmission electron micrograph of the region of the interface between the coating and the titanium substrate, with a larger area of coating being shown in comparison with Fig. 8. Electron diffraction at the region indicated A in Fig. 9 indicates that regions of light contrast consist of amorphous material. EDX analysis of these regions showed mainly the presence of silicon and oxygen. Other regions, of darker contrast, marked B and C in Fig. 8, reveal nanocrystals that consist of rutile according to electron diffraction. The light regions appear to be branched channels or cracks filled with amorphous silica, which extend to the base of the coating.

Results of XRD are shown in Fig. 10 for coatings formed for 300, 900 and 3600 s at 500 mA cm\(^{-2}\), with a duty cycle of 50\% and an \( \text{in}/\text{off} \) ratio of 1. Peaks are evident due to titanium in the substrate and to anatase and rutile in the coatings, with the intensity of rutile peaks relative to the anatase peaks increasing with increased treatment time. Amorphous material gives rise to the broad peak between \( \sim 15^\circ \) and \( 30^\circ \), which increases in magnitude with increase of the
Coatings produced at 500 mA cm\(^{-2}\) using duty cycles of 60% and 70%, with an \(i_{n}/i_{p}\) ratio of 1, were similar to those produced using a duty cycle of 50%, revealing agglomerations of material of dimensions ∼20 to 40 μm at the coating surface and average coating thicknesses of ∼35–50 μm, with morphologies similar to those presented earlier. A duty cycle of 40% resulted in a thinner coating, due to the voltage decreasing and the discharges terminating at an early stage of the PEO process. Other work, examining PEO of a Ti–Al–4V alloy under a high frequency pulsed anodic current with an aluminate electrolyte, also showed an overall decrease in coating thickness with reduction in the duty cycle, but the trend was inconsistent within the investigated range [24,25].

Specimens were also treated in the present study at 500 mA cm\(^{-2}\), using a duty cycle of 50% and \(i_{n}/i_{p}\) ratios in the range 1–1.23. The coating thicknesses at \(i_{n}/i_{p}\) ratios of 1, 1.03 and 1.07 were in the range 40–50 μm, with a relatively minor influence on the coating morphology. Between ratios of 1.13 and 1.23, the thicknesses decreased from ∼35 to ∼10 μm, which correlated with a reduced time of sparking and an increased contribution of the negative current to the total current. The surface of a coating formed at an \(i_{n}/i_{p}\) ratio of 1.13 is shown in Fig. 11(a). The variation in the current ratio caused relatively minor changes in the morphologies of the coatings, unlike PEO of aluminium for which an increase of the ratio of the negative-to-positive current above unity resulted in a transition of the coating morphology to a more uniform, compact structure, as arcs were replaced by “softer” sparking [12,51]. Fig. 11(b) shows the surface of a specimen treated with a duty cycle of 50%, but using a higher current density of 900 mA cm\(^{-2}\) and an \(i_{n}/i_{p}\) ratio of 1. The surface revealed large pores of up to 20 μm
Fig. 7. (a) Transmission electron micrographs and EDX elemental maps of the outer region of a coating formed on titanium for 900 s at 500 mA cm$^{-2}$ in alkaline silicate/phosphate electrolyte, with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratio of 1. (b) Nanocrystals in the circled region of (a). (c) Electron diffraction of the nanocrystals of (b) revealing rutile.

Fig. 8. Transmission electron micrograph of a cross-section of the inner region of a coating formed on titanium for 900 s at 500 mA cm$^{-2}$ in alkaline silicate/phosphate electrolyte, with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratio of, and EDX maps of the distributions of oxygen, phosphorus, silicon, and titanium.
in diameter and nodular coating material. A cross-section showed that the coating was of non-uniform thickness in the range ∼20 to 50 μm. XRD analysis (not shown) indicated the presence of rutile and a large amount of amorphous material, in addition to peaks for the titanium substrate. No anatase or Ti2O5 was detected. The absence of anatase is probably due to an increased temperature of the coating material during PEO at the higher current density, which favours the formation of rutile. The appearance of rutile at higher current densities is consistent with previous reports that conditions that generate higher temperature in the coating favour the presence of rutile, which may form by transformation of anatase [52,53]. EDX analysis of the coating surface revealed an atomic ratio of titanium to silicon of ∼0.05, consistent with a silicon-rich, outer region of the coating.

The coatings produced under all the conditions of PEO that were employed in the present work were relatively porous with rough surfaces. The thickness of the coatings increased with increase of the duty cycle and decreased with increase of the negative-to-positive current ratio. However, the influence of the duty cycle and current ratio on the morphology of the coatings was relatively small. The thicknesses of the coatings were generally limited to a maximum of ∼40 to 50 μm, with extended periods of PEO appearing to result in little increase, or possibly a decrease, in the thickness and an increase in the roughness. Thus, at extended times of treatment, coating material may be lost from the surface due to the action of the discharges. The discharges appear to generate sufficient heat to melt the coating material, with gas generation forming a highly porous morphology. A very porous coating was also reported to form on a Ti–6Al–4V alloy treated in a silicate electrolyte under controlled anodic power density [28]. The coating contained amorphous and crystalline silica, rutile and Ti2O5 according to XRD. The amorphous silica was evident as white material at discharge channels. The formation of the silica-rich region, which was generated under all of the conditions of PEO that were investigated in the study, may be due to a predominance of discharges that occur near the coating surface that result in preferential incorporation of species derived from the electrolyte [14].
3.5. Tribological behaviour

The tribological behaviour of the titanium was investigated in the uncoated condition and following PEO in electrolytes without and with the addition of the ptfe emulsion. The coatings were formed for 900 s at 500 mA cm\(^{-2}\), with a duty cycle of 50% and an \(i_0/\beta\) ratio of 1. This condition appeared to result in coatings of the most uniform thickness, although generally there were no major differences between the coatings produced under the range of conditions that were used in the study. The addition of the ptfe emulsion had no significant influence on the voltage–time response, the coating morphology or the coating thickness, which was in the range 35–40 μm. A scanning electron micrograph of the ptfe particles and carbon fibrils in the dried emulsion is shown in Fig. 12. The particles are of size in the range \(\sim 150\) to 550 nm, and the fibrils of length and width of \(\sim 800\) and 150 nm respectively. The results of TGA measurements on the dried ptfe emulsion and PEO coatings prepared without and with ptfe in the electrolyte are shown in Fig. 13. The dried emulsion underwent a weight loss of \(\sim 12\%\) between 100 and 400 °C due to removal of water, fibrillar carbon and surfactant residues [54]. A decrease in weight by \(\sim 79\%\) occurred between 500 and 600 °C due to degradation of the ptfe [55]. Above this temperature range, the weight decreased slowly up to the final temperature of 1000 °C. The coating formed with ptfe showed significant weight losses at similar temperature ranges to the dried ptfe. The loss between 500 and 600 °C indicates that \(\sim 20\%\) ptfe was present in the coating. In contrast, the ptfe-free coating lost only \(\sim 3\%\) weight from the start of the test up to 1000 °C.

Assuming an average diameter of 300 nm and a density of 2.2 g cm\(^{-3}\) for the ptfe particles, the 5 g dm\(^{-3}\) of ptfe emulsion added to the 1 dm\(^{-3}\) of electrolyte contained \(\sim 1 \times 10^{14}\) ptfe particles cm\(^{-3}\). TGA indicated \(\sim 20\%\) ptfe in the coating, which, for a coating of thickness \(\sim 30\) μm (according to SEM), and of density \(\sim 3\) g cm\(^{-3}\), (assuming a value between that of silica and titania), suggests the presence of \(\sim 1.3\) mg cm\(^{-2}\) of ptfe, or equivalently \(\sim 9 \times 10^{10}\) ptfe particles cm\(^{-2}\), i.e. 0.1% of the particles added to the electrolyte. Owing to the roughness and fine features of the coating, it was difficult to distinguish ptfe particles directly by SEM. However, EDX analysis of the coating surface indicated the presence

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**Fig. 11.** Scanning electron micrographs (secondary electrons) of the surfaces of a coating formed on titanium in alkaline silicate/phosphate electrolyte, with a frequency of 50 Hz and a duty cycle of 50%. (a) For 1200 s at 500 mA cm\(^{-2}\) and a negative-to-positive current ratio of 1.13, (b) For 900 s at 900 mA cm\(^{-2}\), with a negative-to-positive current ratio of 1.

**Fig. 12.** Scanning electron micrographs (secondary electrons) of the dried ptfe emulsion.

**Fig. 13.** Results of thermal gravimetric analysis of the dried ptfe emulsion and of coating material formed for 900 s at 500 mA cm\(^{-2}\) in alkaline silicate/phosphate electrolyte, without and with the addition of ptfe emulsion, with a frequency of 50 Hz, a duty cycle of 50 Hz and a negative-to-positive current ratio of 1.
of significant amounts of fluorine, with a typical point analysis revealing (in at%) of 9% F, 29% Si, 53% O, 6% Ti, 2% P and <1% Na, K.

The results of the ball-on-disc friction tests, under a 5 N load, are presented in Fig. 14 for the uncoated titanium and the PEO-coated titanium with and without ptfe. The coefficient of friction of the uncoated titanium was in the range of 0.45–0.55 during the test of duration 1800 s. The coefficient for the ptfe-free coating was in the range 0.15–0.25 up to 300 s, and then increased to 0.60 at 400 s and further to 0.85 at 1300 s. The value then fell to the range of uncoated titanium when the ball contacted the titanium substrate. The coefficient of friction of the coating formed with ptfe was similar to that of the uncoated titanium. The test was terminated at 690 s, when the titanium substrate was exposed in the wear track. Three replicated tests produced failure of the coating within 100 s of the tests depicted in Fig. 14 and similar coefficients of friction except for the initial ~200–300 s. In this initial period, large fluctuations in the coefficient occurred, which are probably due to the transition between the rough surface of the as-formed coating to the smoother surface of the worn coating, which is shown in later scanning electron micrographs. Subsequent fluctuations occurred due to accumulation of wear debris in the wear track. The ball after the tests of the coating revealed score lines, due to abrasive wear, and small amounts of wear debris, which EDX analysis indicated to be transferred coating material. The coefficient of friction of the uncoated titanium was similar to previous findings for titanium alloys [26,28]. A relatively wide range of coefficients of friction have been reported, typically in the range from ~0.1 to 0.8, for PEO-coated surfaces, depending upon factors such as the conditions of formation of the coating and the wear test parameters, with most studies employing a Ti–6Al–4V substrate [26,28].

The worn surface of the uncoated titanium mainly displayed grooves and irregular cavities along the sliding direction. The presence of grooves parallel to the sliding direction indicated that micro-cutting and micro-ploughing had taken place. The morphologies of the wear scars of the coated surfaces are shown in the scanning electron micrographs of Fig. 15. The tests were stopped at 600 s, before the failure of the coatings. The ptfe-free coating reveals extensive delamination, which is not present for the coating that contains ptfe. The coating material of both surfaces is relatively smooth compared with the original coating surface, suggesting that the contact with the ball had displaced coating material to fill the voids of the relatively rough, original coating surface. EDX point

![Fig. 14. Dependence of the coefficient of friction on time for titanium in the bare condition and following coating for 900 s at 500 mA cm⁻² in alkaline silicate/phosphate electrolyte, without and with ptfe emulsion, with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratio of 1. The ball-on-disc test employed an AISI 52100 steel ball.](image1)

![Fig. 15. Scanning electron micrographs (secondary electrons) of the wear tracks of PEO-coated titanium after a ball-on-disc test for a time of 600 s. (a and b) Coating without ptfe. (c and d) Coating with ptfe.](image2)
analyses were carried out of the coating formed without ptfe at points A, B, and C of Fig. 14(a), corresponding to delaminated material in the wear track, adherent coating in the wear track and the coating outside the wear track. Table 2 shows that the unworn region revealed a high concentration of silicon and low amount of titanium, in accordance with a silica-rich surface suggested by the previous analyses. The adherent coating in the wear track revealed an increased amount of titanium and a reduced amount of silicon compared with the unworn surface, suggesting a reduction in the coating thickness due to wear. The delaminated region had an intermediate concentration of silicon and titanium. Results of EDX line scanning of the wear track of the coating formed with ptfe also revealed a silicon-rich surface, with analyses close to those of Table 2, but with the additional presence of ~9 wt% of fluorine. On either side of the wear track, the fluorine signal showed large fluctuations with local concentrations of up to 60 wt%, probably due to the locally increased concentrations of ptfe particles. In contrast, reduced fluctuations, of up to 18 wt%, occurred within the wear track, suggesting spreading of the ptfe across the worn surface. The worn surface of the coating formed with ptfe is also relatively smooth, with occasional grooves, particles of wear debris, and small cracks.

Fig. 16 shows the wear track following failure of the coating formed with ptfe. Delaminated fragments and detached particles of the coating are evident, together with score lines, indicating abrasive wear, on the regions in the wear track where the titanium had been exposed. After the wear tests carried out for 600 s,
the width and depth of wear scars were measured by optical interferometry. Fig. 17 shows that the greatest depth and width of the track were measured for the untreated titanium, with respective values of 17 μm and 0.64 mm. The lowest values, of ~10 μm and 0.43 mm, were recorded for the PEO coating that contained no ptf, with the addition of ptf resulting in intermediate values of ~15 μm and 0.53 mm. Since the depth and width of the wear scars of the coated substrate are probably partly due to the relocation of coating material as the coating surface is smoothed by the ball, a meaningful wear rate cannot be derived. Although the incorporation of the ptf into the coating reduced the coefficient of friction of the coating sliding against a AISI 52100 steel ball, the durability of the coating was not increased and was poor in comparison with that of coatings formed in other electrolytes [26,28]. Further, the coefficient of friction in the presence of the incorporated ptf was similar to that of the uncoated titanium. Thus, the overall benefits of the coatings to the wear resistance are limited. However, the porosity and roughness of the coating surface may be suited to improvement of adhesion of paint to titanium surfaces. The relatively poor wear resistance of the present coatings can be attributed to the high porosity and the large amount of amorphous silica, which in addition to forming a relatively thick outer region of the coatings also penetrates, and possibly weakens, the inner, titanium-rich region.

4. Conclusions

1. PEO coatings formed at 500 mA cm−2 (rms) in the alkaline silicate phosphate electrolyte, with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratio of 1, are composed of amorphous silica, anatase, rutile, and Ti3O5. Phosphorus species and minor amounts of potassium and sodium species were also incorporated into the coating.

2. The coatings are limited in thickness to ~40 to 50 μm and are highly porous, with a relatively thick, silica-rich outer region and a thinner, titania-rich inner region. The silica is also present in veins that penetrate the inner, titania-rich material. The limitation of thickness is related to a relatively steep drop in the voltage after ~900 s of PEO, with a reduction in the intensity of sparking.

3. Similar morphologies of coatings are generated at duty cycles of 50–70% and with negative-to-positive current ratios of up to 1.13, with thinner coatings being formed at reduced duty cycles and at increased current ratios. The reductions in coating thickness are associated with declines of the voltage and termination of sparking at relatively early stages of PEO.

4. Coatings can also be formed at current densities from 300 to 900 mA cm−2, with a duty cycle of 50% and an i+/i− ratio of 1. Coating formation is not possible at current densities below 300 mA cm−2, with etching of the titanium taking place at a current density of 200 mA cm−2. Coatings formed at a current density of 900 mA cm−2 contain rutile as the main crystalline phase, with no detectable presence of anatase. The coatings also contain a large amount of amorphous material.

5. The coefficient of friction in sliding wear tests of the coatings against a steel ball, using a load of 5 N, is ~0.8 compared with ~0.5 for the untreated titanium. The coefficient of friction when ptf is incorporated into the coating by addition of ptf emulsion to the electrolyte is ~0.4 to 0.5. The rough coating surfaces are initially smoothed by the steel ball, with subsequent growth and linking of cracks causing detachment of flakes of the coating material. The coatings fail at relatively short sliding distances.

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